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THE RECASTING EFFECTS ON THE HIGH GOLD DENTAL ALLOY PROPERTIES

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Abstract

Noble dental alloys are often reused in dental practice by recasting. The aim of this study was to determine if repeated casting of high gold dental alloys has a detrimental effect on alloy microstructure, type of porosity, structure and microhardness. Results showed that recasting procedure had a strong effect on the change of alloy porosity type. It was also found that alloy microhardness increased with the increase of the number of recasting cycles. At the same time the grain growth and changes of the solid solution phases in the microstructure were observed.

Keywords: high gold dental alloy, recasting, microhardness, XRD analysis, alloy porosity

1. Introduction

A vast number of alloys have been used for fixed prosthodontic restorations [1,2]. Diverse factors, such as cost ease of casting and finishing, various mechanical properties, *i.e.* elastic modulus and yield strength, color, accuracy of fit and concerns regarding alloy corrosion resistance are making the adequate alloy selection process quite complex [3]. Dentist is responsible for the conducted prosthetic therapy, which implies the knowledge of composition and properties of a dental alloy after laboratory procedure and before its implantation into the patients' mouth. For decades gold has been used in dental practice to fabricate cast dental prostheses. The interest in using gold or precious noble-metal alloys with a high content of gold, platinum and palladium was due to theirs high corrosion and tarnishing resistance, as well as high biocompatibility. In an attempt to reduce the expense of possible restorations, gold alloys could be subjected to the recasting. Recasting, which comprises the alloy re-melting and re-solidification, may change the composition and structure of these alloys and thus affects alloy mechanical properties and castability, as well as the alloy corrosion resistance [4]. Over the past 20 years the price of gold has risen significantly in the world market. The high price of gold led to a wider use of the precious alloys with a lower gold content, as well as the basic alloys, in dental prosthetics. On the other hand, once melted and cast, precious dental alloys are being remelted and recast in order to be reused in dental practice. It is often impossible to determine the exact number of melting and casting cycles to which alloy is subjected, since it is not possible to determine the exact content of the newly added alloy. A dental alloy repeatedly subjected to melting and casting is likely to change its chemical composition [5]. Some studies showed that the recasting also contributes to the change of the dental alloy biocompatibility due to the lower corrosion resistance of microalloying elements [6]. Literature data, regarding the recasting effects on elemental composition and microstructural characteristics of high gold dental alloys, are very rare [7]. Recommendations concerning the procedure of gold alloys recasting vary from adding no new metal during recasting procedure to adding up to 50% of new metal with previously melted buttons or sprues removed from castings [8].

Even though majority of dentists would choose high gold-based alloys for prosthetic therapy for themselves, there is no rationale reason to claim that the alloy with high gold percentage is biologically inert [9,10]. Therefore, the objective of this work was to investigate the effect of the high gold dental alloy repeated casting on the alloy overall porosity, microstructural properties, crystallographic structure and microhardness, since these properties can affect alloy biocompatibility.

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2. Materials and Methods

Alloy used in this study was a commercial high gold dental alloy with the nominal chemical composition (in wt.%): 75.5-Au, 11.0-Ag, 6.7-Cu, 4.4-Pt, 1.2-Pd, 1.2-Zn. Test samples were prepered using patterns and invested in a mold ring with a phosphate bonded investment for precious alloy. Mold has been preheated for one hour at 750 °C in furnace. Melting was performed at temperature 940 ºC and the casting (t_c = 1120 °C) was performed in a casting machine in accordance with the manufacturer's instruction. The molds were cooled at room temperature and after cutting gating of molds samples were sandblasted. Test alloy samples were cast in the laboratory induction furnace in the shape of small disks with the diameter of 10 mm and thickness of 1 mm. High gold dental alloy samples were examined after a various number of casting cycles, since they were subjected to one (A1), four (A4) and eight (A8) melting and casting sequences.

The alloy structure and properties were investigated using light microscopy (LM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) analysis and microhardness measurements. Samples for microstructural observations were prepared using the standard metallographic preparation techniques. The mixture of 10 ml HNO_3 and 30 ml HCl was used as an etching reagent. The polished and etched samples were investigated using a LM Carl Ziess Axiovert 25 equipped with the digital Panasonic camera WV-CD50 and a SEM JEOL JSM-6460LV equipped with an EDS Oxford Instruments INCA X-sight system. The porosity of recast samples was micrographically determined in the non-etched condition. For that purpose ten micrographs of different sections of each sample were photographed at magnification of 50x. Porosity percentage of the projected area of examined sample was calculated by the quantitative image analysis processing using the standard image analysis technique with adequate computer software (QWin). The grain size of samples (A1, A4 and A8) was determined in etched condition from microphotographs which were taken at magnification of 50x. The grain size has been evaluated using intercept method. Total measured length for all samples was near 50 mm and the number of counted grains was about 300 [11].

XRD analysis was carried out on a Siemens D-500 diffractometar with a Ni filter and CuK_α radiation operated at a tube voltage of 35 kV and a tube current of 20 mA in the theta/2theta mode and at scanning speeds of 0.02 s^{-1} and 0.4 min^{-1}. Microhardness measurements were performed using a Buehler MicroMet 5101 Vickers hardness tester with a load of 300 gf applied for 10 s. Microhardness results were obtained as the average values of ten measurements.

3. Results and discussion

Most frequently observed defect, present on the surface of gold-based alloys, is alloy porosity, which may be caused by two phenomena. The first phenomenon is appearance of the shrinkage porosity induced by the volume decrease during liquid to solid transition, while the second one is the so-called gas porosity which appears as round shiny pores scattered on the alloy surface and in the bulk. These defects cannot be removed by grinding or polishing, because of the possible exposure of other subsurface pores [12]. In the early days of dental casting, presence of shrinkage porosity defects near the sprue attachment points was not an uncommon. Results of numerous investigations demonstrated that it was caused by solidification of the melt in the sprue cutting off the supply of the melt to the main casting while it was still undergoing solidification and contraction [13]. This could be avoided by the selection of appropriate melting temperature, as well as by suitable design and dimensions of the sprue. Nevertheless, even with sprues of good design, it was found that localized shrinkage porosity still persisted in some castings near to their surfaces [13]. In this study change of the alloy properties due to the casting conditions modification is above all indicated with the linear increase of alloy microhardness with the increase of casting cycle number, as it is shown in Fig. 1. Namely, the change of alloy microhardness with the number of recasting cycles follows the ascending order 160 MPa → 179 MPa →194 MPa and after the eighth recast sequence it is observed that the microhardness is increased more than 20 % in regard to its value determined after the first one (Fig. 1). Further, it is well known that linear contractions of at least 1.25 % can be expected during the liquid to solid transition of the dental noble alloys [14], which in turn influences the alloy porosity occurrence. Change of the overall porosity (including shrinkage and gas porosity) of the recast high gold dental alloy and the typical dendritic microstructures of the recast alloy samples are shown in Figs. 1 and 2, respectively. Two types of porosity may be distinguished, *i.e.* the presence of shrinkage porosity is dominant after first recasting sequence (Fig. 2a), while in the other samples the presence of gas porosity is clearly revealed (Figs. 2b and c). Porosity varies from 0.4 % for A4 sample to 0.9 % in the case of A1 sample**.** The increase of gas porosity is mainly connected with the reduction of zinc content in the alloy. Namely, it is well known that during multiple melting and casting comes to reduction in the content of the zinc and copper. Zinc acts as an oxygen scavenger during melting to minimize the oxidation of the other elements in the alloy. Zinc prevents oxygen from forming gas porosity in the casting [4]. The grain growth with recasting was also detected (Figs. 2 and

3). The change of average grain size and the number of counted grains with increase of number of recasting were given in Table 1.

Table 1. *The average grain size and number of counted grains in A1, A4 and A8 samples in as-cast condition.*

Sample	A1	A4	A8
Mean grain size (μm)	179.4	249.7	274.3
Counted grains	313	233	225

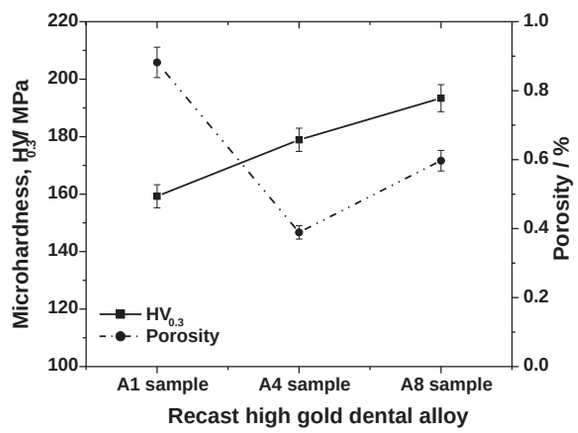


Figure 1. *Recasting effect on the microhardness and porosity of the high gold dental alloy.*

Presence of the pores at the A4 alloy sample grain boundaries was distinguished (Fig. 3b) due to the higher content of impurities and oxides, which are sites of first corrosive attack during etching.

EDS analysis of all samples was conducted and in that purpose several different positions in the same grain were analyzed, as it is shown in Table 2. The EDS point analysis indicates the presence of the chemical composition inhomogeneity between two adjacent grains, especially when platinum, palladium and zinc are concerned.

Recasting results in appearance of the new grains with size that may differ from the original one (Table 1). When the melting temperature and casting conditions are maintained uniform, *i.e.* the same for all samples as it is the case in this study, the new grain size depends mainly on the concentration of the grain formation nuclei. Although generally the impurities may facilitate grains nucleation, which might lead to the decrease of the grain size, in this study the grain size increased with each consecutive recasting sequence (Fig. 2). For example, Horasawa and Marek observed that in the case of the silver-palladium alloy the grain size has increased steadily with the increase of the number of recasting cycles [4]. Concentration of inclusions and impurities, such as oxides, nitrides and carbides, rapidly increases during the multiple casting of the noble alloys resulting in the microhardness increase (Fig. 1). Bearing this fact in mind, it may be concluded that the increased concentration of impurities during multiple casting may be regarded as a rather important factor influencing the increase of microhardness. These impurities act as a barrier to dislocation motion

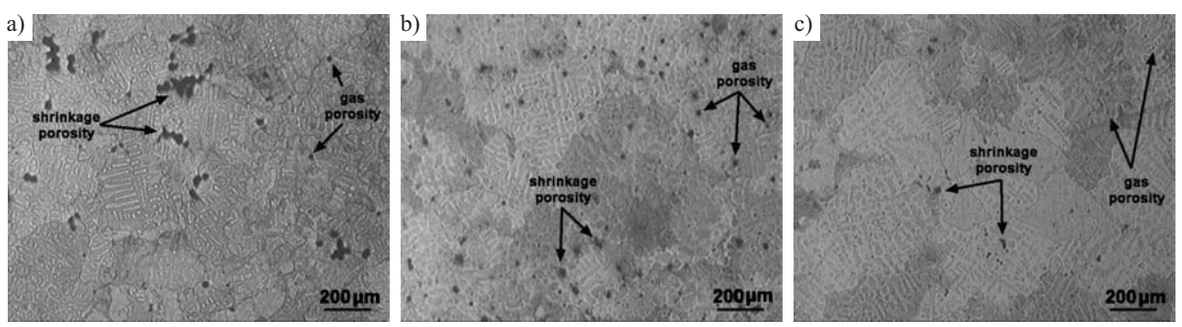


Figure 2. *LM micrographs showing microstructure of the high gold dental alloy. (a) A1, (b) A4 and (c) A8 alloy samples.*

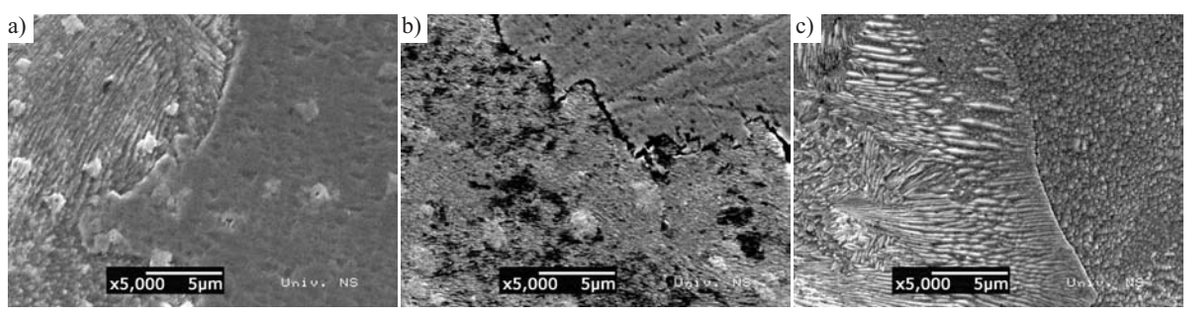
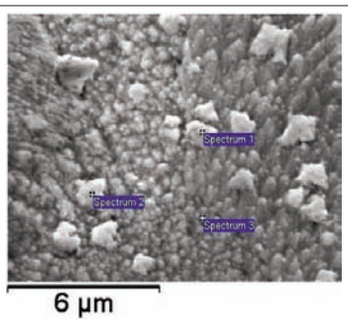


Figure 3. *SEM micrographs showing microstructural features and grain boundaries of the high gold dental alloy. (a) A1, (b) A4 and (c) A8 alloy samples.*

Table 2. *The chemical composition of the single grain (in wt.%) determined by EDS analysis.*



Spectrum	Chemical composition / wt.%					
	Cu	Zn	Pd	Ag	Pt	Au
1	6.93	0.65	-	11.68	-	80.74
2	6.61	1.15	-	11.23	1.26	79.75
3	5.78	0.99	1.53	9.94	2.53	79.23
Mean	6.44	0.93	0.51	10.95	1.26	79.91
± s.d.	± 0.59	± 0.26	± 0.88	± 0.90	± 1.26	± 0.77

causing the hardening of the matrix [4]. In the same time, solid solution effects must not be neglected.

Investigated high gold dental alloy is multiphase alloy, since it contains different elements with different chemical affinity. Every change in the elements ratio influences change in the alloy structure and properties. Gold-silver, gold-palladium and gold-platinum form solid solutions in all proportions. On the other hand, the ratio of silver and copper is very sensible because silver and copper have limited solubility in the solid state.

The XRD patterns of the alloy samples subjected to the recasting are shown in Fig. 4. As can be seen, peaks characteristic for gold-palladium-platinum solid solution are present in the XRD patterns and correspond to $Fm\bar{3}m$ cubic crystal structure. The intense peaks observed at approximately 40°, 45°, 66.5°, 80° and 84° represent (111), (200), (220), (311) and (222) Bragg reflections, respectively. With the increase of the casting sequence number, intensity of gold rich solid solution peaks changes and some peaks completely disappear after the eighth recasting cycle (peaks which correspond to the reflections from the (200) and (311) planes). However, XRD analysis of the alloy sample after eight consecutive recasts revealed presence of the palladium rich solid solution (Fig. 4). The crystallite size of the gold-palladium-platinum rich solid solution was calculated for all samples (A1, A4 and A8) using line broadening information and Scherrer's formula. The crystallite sizes were calculated using peaks broadening profile of (111) peak at $2\theta \approx 40^{\circ}$ and Sherrer's formula given in Eq. 1:

$$d = 0.9\frac{\lambda}{\beta\cos\theta} \quad (1)$$

where λ is wavelength (1.5418 Å) and β is full

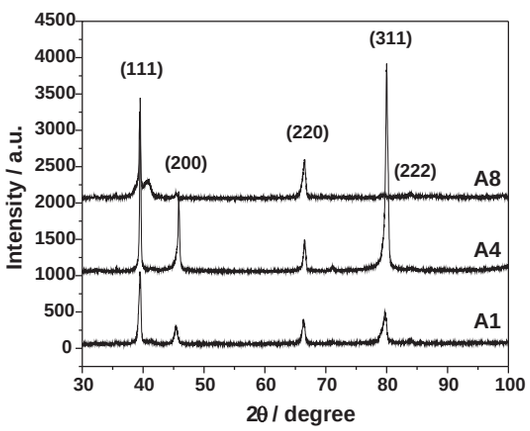


Figure 4. *XRD analysis of A1, A4 and A8 alloy samples in the as-cast condition.*

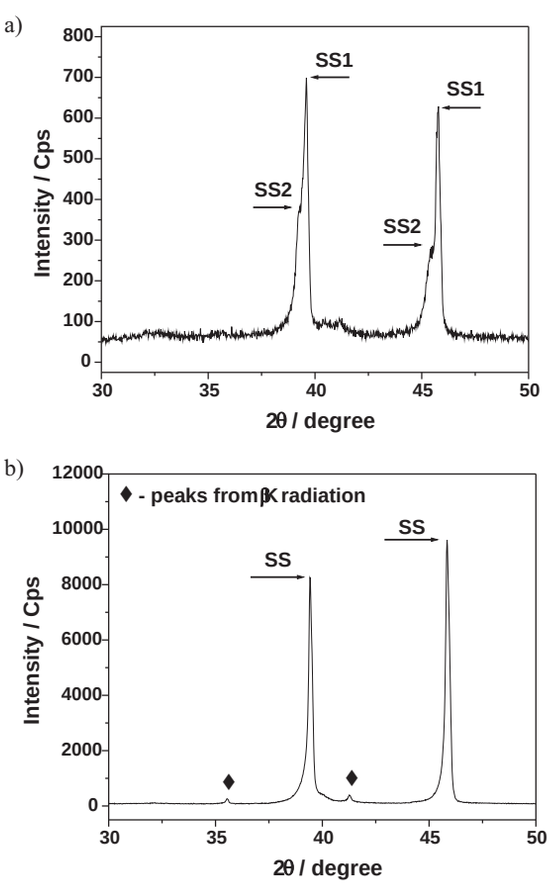


Figure 5. *XRD patterns of (a) A4 and (b) A8 alloy samples obtained using the slow scan mode.*

width half maximum (FWHM) of the corresponding peak. The calculated crystallite sizes of the all obtained gold-palladium-platinum solid solutions are around 17 nm, as it was reported in the literature [15-18].

Further XRD analysis showed (Fig. 5a) that after the fourth recasting sequence two solid solutions are present in the alloy microstructure: gold-palladium-platinum solid solution (SS1) and platinum-silver solid solution (SS2). On other hand, further increase of the casting sequence number causes separation of the gold-palladium-platinum rich solid solution (SS) (Fig. 5b). Thus, it is reasonable to suppose that disappearance of some peaks and appearance of SS1 and SS2 solid solutions peaks on the recorded alloy XRD patterns, together with increased concentration of impurities, may also affect the increase of alloy microhardness (see Fig. 1) during the increase of casting sequence number (A4 and A8 samples).

4. Conclusions

From the presented results it can be concluded that the recasting procedure changes the microstructure, crystallographic structure and microhardness of the high gold dental alloy. Microstructure analysis showed that the grain growth occurred during recasting and that two types of porosity were distinguished. The microhardness increase was induced not only by the increase of impurities concentration, but also by the disappearance and appearance of different phases during recasting sequence. Generally, results of this study indicate that this type of high gold dental alloy may be safely used in recast condition only after it was subjected to a small number of recasting cycles. Further investigation will be focused on the corrosion behavior of a high gold dental alloy after repeated casting.

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